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# **FIRST GET-TOGETHER OF RESEARCH AND INDUSTRY**

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**Glass, Ceramics, Enamels, Clays  
and Refractories, Mica**

**WORKING GROUP 12**



**COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, NEW DELHI**





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## CONTENTS

Urgent Problems Facing the Refractory Industry	...	1
D. R. SUBRAMANIAN		
Research & Industry in Refractories	...	5
P. K. PAUL		
Raw Material Situation for the Production of Basic Bricks	...	7
J. D. PANDA		
Substituting Magnesite by Seawater Magnesia in the Manufacture of Refractory Magnesia	...	12
B. K. SHUKLA & R. N. VOHRA		
Sorel Cement	...	14
B. K. SHUKLA & P. M. TRIVEDI		





# Urgent Problems Facing the Refractory Industry

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D. R. SUBRAMANIAN

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## Raw materials

**Fireclays.** While there is no dearth of fireclays in India suitable for the manufacturers of moderate heat duty refractories, the type of clays suitable for making blast furnace refractories is not readily available. Fireclay seams carrying high alumina and reasonably free from impurities, occur very often mixed with ordinary quality clay and the seams are usually thin — anything from 1 ft to 4/5 ft; thick seams 6 ft and over are very rare. Very selective mining is therefore necessary at all levels to obtain the clays suitable for the manufacture of blast furnace bricks. This is a very sad state of affairs and if India is to succeed in making itself self-sufficient in the manufacture of blast furnace bricks, extensive field research is necessary to locate such clays and having located such clay seams there should be some means of enforcing that such clays do not get mixed up with inferior clays and used up for lesser purposes. If necessary, there should be legislation to prevent such misuse, in the same way as selected 'A' grade coal is now controlled by the Government.

If this is not done the only alternative for the industry would be to resort to the use of washed china clays which will not only make the bricks very expensive but also mean considerable modification to the existing refractory plant — before china clay can be handled to make blast furnace bricks.

**Chromite.** At the moment the type of chrome that is being used for refractory purposes is really a metallurgical grade carrying something like 52 per cent of  $\text{Cr}_2\text{O}_3$ ; no country in the world is using such chromite for refractory purposes and it is only a question of time before this type of chromite is commandeered by the metallurgical industry. The other known chrome deposits which can be classified as refractory chromites are far too high in iron and give considerable trouble, both in manufacture and perhaps in subsequent use. Field work is necessary to locate reasonably low iron refractory grade chromite. The iron expressed as  $\text{FeO}$  should not be more than 16/17 per cent and silica not more than 5 per cent and only traces of fluxes are like lime. The actual content of  $\text{Cr}_2\text{O}_3$  can be flexible, but to keep the other impurities down it is desirable to have a  $\text{Cr}_2\text{O}_3$  content of not less than 45 per cent.

**Magnesite.** The only industrial source of magnesite at the moment is the Salem deposit. The Almora property has not yet been developed. While the resources at Salem are very extensive, it must be remembered



that the occurrence of the magnesite is such that it is intimately mixed up with silica in thin layers. So far, the only process adopted for beneficiation is by cleaning manually. This is a very laborious and labour consuming process and the efficiency of the process is deteriorating very fast, partly because it is becoming more and more difficult to extract dependable work from the labour and partly because the cost of this job is going up by leaps and bounds. It is obvious that a mechanized process of beneficiation is very urgent; obviously this would need a change in the layout of the existing plants which are essentially designed to handle coarsely crushed crude magnesite and cannot handle all the magnesite in the form of dust. Therefore, if the beneficiation process means that the magnesite has to be recovered in the form of dust, a briquetting plant is necessary.

Even if the Almora property is developed, I do not think that we can escape either selective mining of beneficiation because there will always be some contamination of dolomite in the Almora deposits.

The impurities in the magnesite have to be particularly considered in the light of the demand that is being made by Bhilai Steel Works for the so-called direct bonded basic bricks for the steel furnace roofs. I doubt very much if with the type of impure raw materials available in this country, we could succeed in making a direct bonded brick in bulk. First of all, direct bonding implies that a brick will contain as small a quantity as possible of a silicate matrix, otherwise the bond will not be a direct bond between chromite and magnesite, but will be through a medium of a silicate bond. A brick containing high silica impurities may not stand the high temperature firing that is required for direct bonding. Even assuming that we ignore the silicate matrix of high fired bricks in bulk, the manufacture will become a very difficult problem with high silica materials. All other steel manufacturers in India are taking up chemically bonded basic bricks in replacement of silica in steel furnace roofs. It is obvious therefore that on this point an exchange of views among the steel workers is very necessary.

**Bauxite and quartzite.** I do not think quartzite offers any problem. In any case the importance of silica has gone out except for coke oven bricks and bauxite of different refractory grades is available in the country. It will be only a question of making the railway rates realistic to make it within economic reach of the manufacturers of refractories. This particularly refers to the better grades of bauxite which occur only in Saurashtra, whereas the major refractories are all situated in eastern India.

### **Coke oven silica bricks**

Even though silica has been displaced by magnesite for steel furnace use, silica is still necessary for coke ovens. The making of silica coke-oven bricks is a specialized job and requires careful handling. Most of the ovens of Tata's and IISCO's have been built with Indian bricks and therefore there can be no question of any doubt of the local bricks being suitable for such jobs. But, Indian manufacturers are only equipped to make limited quantities of coke-oven silica and the reason is obvious. Once a coke oven is built, it is expected to last twenty years and therefore there is no question of any large scale operational requirements. While the argument may be put forward that in our growing economy, more and more enquiries may be coming through and there are already about



thirty batteries in India, one has to remember that there are a number of different designs of batteries and there are no standards. The building of coke ovens is invariably a turn-key job and each contractor has his own design. Considering that each battery involves something like 600 different shapes, the magnitude of the moulds and dies which have to be handled by the manufacturers is really colossal. No factory in India can afford to make silica coke oven bricks in large quantities at short notice. Both Tata and IISCO plan their requirements well in advance and they even stagger their requirements by mutual arrangement if necessary so that the industry can cater to their requirements from indigenous sources. A manufacturing period of about two years is necessary, during which period the bricks must be checked by the purchaser and stocked in his own yard.

### **Pouring refractories**

There is a very wide difference of opinion on the types of pouring refractories demanded by individual steel makers. Tata use the low P.C.E. American type bloating nozzles and stoppers. IISCO like the English nozzles and stoppers which are also bloating but much more refractory than the American type. The Germans use ordinary refractory type nozzles and stoppers — the quality of which is akin to our IS6. Bloating type of clays have not yet been properly investigated in this country. This is a work which the research laboratories could take up immediately. Apart from the composition, the method of manufacture plays a very major part in the production of articles of uniform quality. Since these are vital items in the ladle equipment, uniformity of the quality should be the prime requirement otherwise the operational results will be very erratic. The research workers should in my opinion devote as much time for this aspect of this problem as for the composition of the articles. Bhilai Steel Works have been using basic nozzles and they appear to be quite happy with them. Considering the divergent views on the part of the consumers it would be necessary to arrange for an exchange of views and try to bring about a uniformity in the demand in the first instance.

### **High alumina bricks containing 75% or more of $\text{Al}_2\text{O}_3$**

There is a growing demand for this type of brick for lining the reheating furnaces and also the ladles of continuous casting process. The industry has only recently taken up this work and if bulk supplies are made available it would be advisable for the research laboratories to follow this up.

### **Fosterite**

Bhilai Steel Works is the only place where fosterite is being used for the steel furnace checkers and if it is really better than the other types of checkers both in performance and cost there is no reason why the other Steel Works cannot take advantage of their experience, but an exchange of views is very necessary. A number of various types of dunites are available in this country and the research laboratories have also produced fosterite bricks. The industry has also produced bulk samples for test



but the complete reports are not yet available; the research workers might follow this up.

### **Glass works refractories**

It is advisable for one or two refractory manufacturers to specialize in glass works refractories. At the moment everyone is making every type and since the steel works requirements are heavy the glass works refractories often get a step-motherly treatment. This can only be remedied by a few manufacturers specializing in glass works refractories provided the glass makers agree to cooperate.

### **Equipment**

Some of the refractory manufacturers need certain balancing equipments to take up some of the specialized lines of work indicated in this note and to eliminate imports of these items it would be far cheaper to give facilities to the indigenous manufacturers to import the balancing machinery than to import specialized refractories continuously year after year.



## Research & Industry in Refractories

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In recent years it has been realized as axiomatic that research and development are the keys to industrial progress. Every one emphasizes the importance, the Managers of Industry, the Economists and very recently the Politicians. I would like to stress to what extent it has been achieved in the Refractory Industry during the last few years, especially with sudden growth of steel industry, in which the refractories consumption alone is to the extent of 75 per cent of the total output.

Growth is not necessarily a measure of efficiency. In refractories the longer the service performance, the smaller the tonnage required. The impact of change of iron and steel technology necessitated for better quality materials. The steel production at present is fourfold but the consumption of refractories has not markedly changed. Though in the beginning the estimated consumptions are very high, now it is realized that the figures are not very realistic.

In few years, our refractories industry has made several developments with the help of National Metallurgical Laboratory and Central Glass & Ceramic Research Institute of CSIR. The development & research work can be done by national laboratories, by the industries themselves and by the consumers and lastly by the universities. Unfortunately in our country not much applied work is carried out by the universities. I feel that we should get more benefit from universities, where young graduates can tackle the problems. Ideally, the scientists engaged in basic research at university could follow the pursuit of knowledge either for science or technology. But the technology must be applicable. The universities should be in close touch with industry and the work done should be sponsored by industry.

When we commissioned our one million tonne Plant, at the time of construction considerable amount of refractories were imported. For sometime we did import the materials for normal maintenance, and at the same time we had to develop the products to substitute the imported ones. The matter was taken up with refractories industry by giving them samples and encouragement by making trials in actual service performance. This initiative has led us to achieve the goal, but we cannot say boldly that we have attained the desired object. With rapid changes in steel technology, we have to pursue for new and better quality material all the time.

The development of graphite crucibles, low grade chrome refractories, bladed kynite bricks and so many other products by NML, the recently

developed product of 95% alumina bricks by CGCRI are commendable. One thing I would like to stress here is that these products developed should be produced on a pilot plant scale and we will be pleased to try them and assess the performance. The scientists should follow how their product is behaving in a particular location, under what conditions and its ultimate behaviour, so that there is a possibility for further improvement work. We may mention that very little work in these lines is being carried out by the Industry. I can imagine their difficulties, for instance, they may not have all the technical facilities for post-mortem examinations.

The development of products, both by the industry and by laboratory has helped us in eliminating imports and I am pleased to inform that our imports are nil this coming year.

With ambitious steel production programme, the new methods of steel technology will come into picture.

I understand there is a great irregularity of supply of raw materials. Generally, the traditional raw materials from mother earth are impure. In the present state, purity is not the criterion, but consistency and uniformity. It is high time that our mining methods should be changed and more systematic and scientific methods should be adopted. This can be possible only if the Government enforce strict measures.

### **Magnesia**

Today I find difficulties in getting magnesia of the desired specification, and the cost is going up. By the end of Fourth Plan I can visualize that we have to get magnesia only from seawater of pure quality and that quality is warranted for so many applications, for refractories manufacture and for ramming materials. Though the capital expenditure is high but it will pay back in the long run, like in other countries.

### **Alumina**

The trend is for using higher alumina bricks with desired properties. We have to explore the possibilities of developing good raw material and the economic usage.

### **Zirconia**

This type of material would be of great importance in casting pit ware, when we switch on to continuous casting.

### **Technical personnel**

It is not out of place to mention the need of technical personnel in industry. With rapid change of technology and the new methods to be adopted, highly qualified Ceramic Engineers are needed in the industry. A qualified engineer will soon think of producing better quality ware and implement new methods. At present, I wonder, how many Ceramic Engineers are not properly placed in the industry.



## Raw Material Situation for the Production of Basic Bricks

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During 1963-64, 467,700 Nos. of magnesite bricks and 55,000 Nos. chromite bricks have been imported into India at a value of Rs 2.2 million. This does not include the mag-chrome bricks imported by Bhilai Steel Plant which amounted to 6378 tons during 1963-64.

The corresponding import figure for 1964-65 was 128,240 Nos. of magnesite brick at a value of Rs 7.5 lakhs which also does not include the mag-chrome roof bricks of 2,500 tons imported by Bhilai Steel Plant.

The figures given above do not include the basic bricks imported under package deal which in itself is very high. We know from a particular instance where 3 years' consumption of magnesite bricks occurred with the L.D. converter and the same has been included in the price of the plant by the supplier.

The basic bricks were up till now imported because probably the consumers feel that the quality of the indigenous product is not up to the standard of the bricks normally used. But before comparing the quality of the imported and indigenous bricks on the basis of the test results supplied by the manufacturers one should take into consideration many factors such as: (a) the raw material available in the country from where the bricks have been imported, (b) the place of use of such refractory material and whether any alternative indigenous product can be used instead, and (c) the raw material situation for the manufacture of indigenous product.

It is the aim of the present paper only to deal with a very important raw material required for the manufacture of basic bricks on which very few fundamental studies have been made. It is not possible for individual manufacturers to make such studies as they have only a few equipments and also the source is limited for this purpose. Last but not the least due to the import restriction the individual commercial firms are not able to procure the instruments they desire for their research work.

In foreign countries, such fundamental research work which is helpful for the growth of industry is either tackled by the Institute organized by a group of manufacturers as for example German Research Association or by institutions affiliated to the universities.

### **Magnesite raw material**

Magnesite occurs mainly in two forms: (a) Crystalline magnesite, (b) Compact magnesite.

The compact magnesite or the crypto-crystalline variety of magnesite has been decomposed from magnesium silicates like serpentine or olivine by carbonate water. Naturally their principal gauge material is serpentine or olivine. Because of their low iron and low calcium oxide content, it was difficult to sinter at lower temperature and therefore they were generally used for the manufacture of sorel cement in chemical industry and cellulose industry. In Europe as well as in America, the occurrence of this magnesite was rare until recently. In 1951 by chance a big deposit has been discovered in Yugoslavia and in Greece and some parts of Austria<sup>1</sup>. Therefore until recently, their use has been restricted to the manufacture of low calcined magnesia and not often for the manufacture of refractory bricks.

The crystalline magnesite which is a metamorphic form of limestone is formed after coming in contact with magnesium-containing thermal spring. As there is a continuous transition of magnesite,  $\text{MgCO}_3$  to siderite  $\text{Fe}_2\text{CO}_3$ , in addition to calcium they have also iron as their impurities. The iron rich magnesite is called Breunnirite<sup>2</sup>. The important and biggest deposit of this type of magnesite is in Austria, Steirmark, Karnten, Veitsch, Radenthein etc. This type of magnesite was first used as the refractory material because it could be sintered at lower temperature. This property is due to the high impurity iron content. The Austrian magnesite can be divided therefore in 3 qualities, magnesite with more than 3%  $\text{Fe}_2\text{O}_3$ , up to 3%  $\text{Fe}_2\text{O}_3$  max. and between 2 and 3%  $\text{Fe}_2\text{O}_3$  in the raw stage. Because of this low sintering property Austria was the highest producer of magnesite in 1930.

During the war Britain and USA could not get raw or calcined magnesite from Austria. Therefore they tried to get magnesite from seawater which is the unexhaustible source for magnesia as it has been calculated that one cubic mile of seawater contains 6 million tons of magnesia. This is a pure magnesite obtained by synthetic process containing less than 1-2%  $\text{SiO}_2$  and 1-2% lime. Half the production of magnesite in USA and the most of UK supply comes from seawater<sup>3</sup>.

Considerable research work has been done on the crystalline variety of magnesite specially the sintering property, the formation, the effect on slag attack etc., because of its availability and low sintering property. With the advancement of science and technology the higher temperature sintering of magnesite specially with the less impure seawater magnesite has been proposed and the behaviour, crystal growth and slag attack have also been studied in advanced countries like Great Britain and USA — their land of origin.

But unfortunately very few fundamental studies have been done on the crypto-crystalline variety of magnesite because probably of their occurrence in particular underdeveloped countries like Yugoslavia, Greece and India. The fundamental study on Indian magnesite has been done by Chesters and that too even only the resistance to hydration with calcining temperature. He has found that the Indian magnesite even containing 5.4%  $\text{SiO}_2$ , 0.7%  $\text{Fe}_2\text{O}_3$  and 2.6%  $\text{CaO}$  sinters at a temperature of 1600°–1650°C. giving a crystal size of 0.04–0.05 mm. with a very small hydration tendency even without addition of iron. According to Chesters the well sintered magnesite must have crystal size of 0.03 mm.<sup>4</sup>. Konopicky<sup>5</sup> has made some fundamental research work on the compact magnesite in 1937 and found that it is necessary to add  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  or preferably calcium-ferrite in order to get a better sintering property at the temperature the shaft and rotary kilns were operated at the time. But the



sintering temperature of Indian magnesite at present is between  $1650^{\circ}$  and  $1800^{\circ}\text{C}$ . which is much more than the temperature mentioned by Chesters<sup>4</sup> in his experiment.

The problem faced by the basic brick manufacturers at present is to get raw magnesite of desired quality to produce refractory materials in order to satisfy the Indian Standard Specification IS:1749-1961<sup>6</sup> for magnesite refractories for steel plant and IS:1750-1961<sup>7</sup> dead burnt magnesite only in respect of the silica content. The  $\text{SiO}_2$  content of magnesite according to above-mentioned specification is highest, 5.5 per cent. All the three basic brick manufacturers draw their supply of raw material and dead burnt magnesite from Salem area. Nature of the occurrence is same in this place. The silica content of the raw magnesite must be kept maximum 2 per cent because it has been already the experience that the  $\text{SiO}_2$  ratio in dead burnt magnesite to raw magnesite is 2.2–2.4. This is probably due to the loss of light calcined magnesite through the chimney and trap door as the low calcined magnesite is much more finer in size than the corresponding olivine or serpentine at that temperature.

During production of dead burnt magnesite one gets peas of size above 1 mm. up to 10–50 per cent and dust below 1 mm. between 30 and 50 per cent, depending upon the operation. It has been also our experience that the dust contains 2–3 per cent more silica than the peas. If one has to produce peas according to above specification, i.e. maximum 5.5 per cent  $\text{SiO}_2$  than the dust obtained from the same is useless for the manufacture of refractory bricks.

It has already been the experience of the basic brick manufacturers and the raw magnesite suppliers or miners that the pit rejection is as much as 20–25 per cent during mining even if one takes extra care. After the raw magnesite is mined, the nature of the ore is such that the high siliceous material containing magnesite and the relatively pure magnesite are embedded in each other and the separation is not only problematic but also very costly. The chipping rejections at this stage varies from 25 to 50 per cent. After calculating the loss in sintering, one gets only 1 to 1.2 tonnes of dead burnt magnesite peas and dust together out of 8 tonnes of raw magnesite mined.

Now the question before us is: (a) Is it necessary to limit the silica content of dead burnt magnesite peas and magnesite brick to 5.5 per cent? (b) What steps one can take to recover the national loss of 70–80 per cent of raw magnesite during the production of dead burnt magnesite? The first question has been studied by us from the manufacturer's stand point of view.

We made trials by making magnesite bricks with dead burnt magnesite containing about 9 per cent  $\text{SiO}_2$  which gave the following property:

*Chemical analysis*

$\text{SiO}_2$	9.2%
MgO	88%

*Other properties*

B.D.	2.81
T.P.	20.4%
A.P.	20.0%
R.U.L.	Over $1700^{\circ}\text{C}$ .
Sp. gravity	3.53
C.C.S.	640 kg./cm. <sup>2</sup>

From the above, one can see that all the conditions maintained in the IS specification are satisfied by this brick except the  $\text{SiO}_2$  content and it gives a very high RUL, figure not generally expected from a high silica material.

A thin section and polished section of the brick was analysed under the microscope. The petrographic analysis of the thin section and also by the help of etching method developed by Konopicky and Trojer on polished section, it is revealed that the periclase crystals are cemented by forsterite thus giving a better bonding than the periclase-periclase bonding even at higher temperatures thus showing higher RUL values.

The crystal size of the periclase in the dead burnt magnesite peas are as high as 40–50 $\mu$ .

For convenience the melting point of the different crystals as occurring in magnesite with impurities are given below<sup>1</sup>:

	°C.		°C.
Periclase, MgO	... 2640	Dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$	... 2130
Magnesium ferrite, $\text{MgO} \cdot \text{Fe}_2\text{O}_3$	... 1750 (about)	Tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$	... 1900
Spinell, $\text{MgO} \cdot \text{Al}_2\text{O}_3$	... 2135	Dicalcium ferrite, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$	... 1435
Forsterite, $2\text{MgO} \cdot \text{SiO}_2$	... 1890	Brownmillerite, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	... 1415
Monticillit, $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$	... 1500 (about)	Free lime CaO	... 2570
Merwinit, $3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	... 1577		

It has also been stated that in the absence of CaO, the silica combines with magnesite to form forsterite which is the case with our Indian compact magnesite of Salem in which the lime content in the raw state is as low as 0.5 per cent<sup>8</sup>. In the presence of lime in the ratio  $\text{CaO} : \text{SiO}_2$  more than 1.87 dicalcium silicate and tricalcium silicate is formed whereas if the  $\text{CaO} : \text{SiO}_2$  ratio is less than 1.87 it has been found that low melting substance like montecellit or merwinnit are formed<sup>9</sup>. As has been already discussed, this is only the case with crystalline magnesite whereas with high silica content compact magnesite with such a high temperature of calcining we found only the presence of forsterite as the binding material which is also evident from the RUL figures. In the case of magnesite as occurred in Austria, one has found also that the di and tricalcium silicate does not promote any crystal growth rather the dicalcium silicate decomposes while cooling, thus weakening the periclase bond<sup>8</sup>. It is therefore necessary for them to have higher amount of iron oxide to give the cementing property by the formation of magnesio ferrit. But one cannot avoid the formation of low melting substances such as calcium ferrit or fialite in presence of silica or brownmillerite in presence of alumina if iron oxide is present<sup>1</sup>.

We are therefore of the opinion that the  $\text{CaO} \cdot \text{SiO}_2$  ratio is not to be maintained or very high amount of iron oxide is not to be added for such crypto-crystalline variety compact magnesite with high silica content as it occurs in Salem, specially when the calcining temperature is so high and also it does not matter if the silica content in the magnesite is little higher than specified by the IS specification.



So far as the slagging action is concerned, only one literature could be cited where the action of iron oxide and titanium oxide on forsterite their melting point and phase relationship has been studied<sup>10</sup>. But how far the open hearth slag will effect the magnesite with such a well distributed forsterite bond, no one has yet studied. This must be done in comparison with the magnesite produced in Austria and other countries.

A lot of saving of the available national resources of raw magnesite can be made if the use of dead burnt magnesite peas and magnesite bricks having high silica content is accepted by the consumers and the specifications for both these items are suitably amended as far as  $\text{SiO}_2$  content is concerned which we feel, will hardly affect either the quality of steel produced from these furnaces or reduce the lining life.

**Beneficiation of raw magnesite.** Further in order to save the national loss and to conserve the magnesite deposit one should find a solution of beneficiating not only in a laboratory scale but also give a design of the plant for this purpose with the costing so as to attract the commercial firms to exploit the same.

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# Substituting Magnesite by Seawater Magnesia in the Manufacture of Refractory Magnesia

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It is estimated that 12 to 20 kg. of basic refractories are consumed per tonne of steel produced. With improvement in steel making, there is a gradual shift in the use of refractories from acid to basic. The total production of dead burnt magnesite refractories in 1960 was only 64,200 tonnes. With increase in the production of steel the gap between the supply and demand continued to widen. The panel on refractories, Ministry of Commerce and Industry, Government of India, estimated a likely demand of 90,000 tonnes of dead burnt magnesite refractories and accordingly recommended an installed capacity of 1,12,000 tonnes during the Third Plan period<sup>1</sup>. The country imported magnesite bricks and shapes worth Rs 8 lakhs during 1964-65. At the same time India exported a small quantity of magnesite bricks and shapes to some ECAFE countries. There is thus a considerable scope for expansion of this industry not only for meeting the internal demand but for exports as well.

At present all the basic refractories are made from magnesite. The reserves of magnesite are spread over in different parts of the country, and are estimated to be 104 million tonnes. The deposits of Madras and Bihar are of high grade magnesite suitable for refractories. But our reserves are small compared to those of China (5000 million tonnes), Korea (3000 million tonnes) and New Zealand (600 million tonnes)<sup>2</sup>. In view of the high quality of Indian magnesite there is a good demand in other countries. During 1964-65, India exported calcined magnesite worth Rs 2.3 crores, to European and Asian countries.

In view, therefore, of the facts that our reserves of good grade magnesite are not inexhaustible and there is an expanding market for our high grade magnesite ores, there is a need for tapping an alternate source for the supply of magnesia of various grades. In USA, although the reserves are estimated to be 66.2 million tons, synthetic magnesia to the extent of 3.2 lakh tons was manufactured in 1960.

The alternate method refers to the use of magnesium of seawater. The magnesium of seawater can be made use of in two different ways, one is to precipitate magnesium hydroxide from soluble magnesium salts by the use of calcined limestone or dolomite. The other is the thermal decomposition of magnesium chloride wherein along with magnesium oxide, hydrochloric acid is obtained as a by-product. The raw materials for the precipitation process are soluble magnesium salts and limestone or dolomite.



India has a long coastline of 3500 miles. At many places along the coast there are a large number of salt works. The coast of Saurashtra and Kutch is a major salt producing area. In the south and east coast there are salt works near Tuticorin, Madras and Calcutta. These salt works produce bittern as a by-product which is rich in magnesium salts. Alternately direct seawater can be used as a source of magnesium. The other raw material, viz. limestone or dolomite, is available in sufficiently large quantities. There are large reserves of high calcium limestone in Saurashtra, Rajasthan, Madras and Kerala. In Saurashtra, the high grade limestone deposits are near Gourkhamadi, Porbandar and massive corallite occurring in the sea bed in the Okhamandal area. In Rajasthan, high grade limestone estimated at more than 1 million tons is available near Gotan, Sojat and Ghotra. In Madras and Kerala, the high grade limestone deposits estimated at 2-3 million tons are available near Pandalkudi, Palavanatham and Ramianpatti.

Although the process for the manufacture of precipitated magnesia is generally known, the exact technical details are to be worked out, especially in view of the utilization of indigenous raw materials. Such plants can produce magnesia not only for the refractory purpose but also the caustic calcined magnesia for oxychloride and other industries as well as the pharmaceutical grade magnesium hydroxide. Again by suitable additions, other industrially useful compounds like basic magnesium carbonate and moulded articles from 85 per cent magnesia for thermal insulation can also be prepared. The major part of the equipment needed for such a plant like rotary kiln, lime slaker, thickeners etc. can be fabricated in India.

For the manufacture of 1 ton of magnesium oxide 2.7 tonnes of limestone and 0.7 m. litres of seawater are required. The export cost of caustic calcined magnesia is between Rs 270 and Rs 320 per tonne and according to our estimates for a plant producing 5 tonnes of magnesium oxide per day, the cost of seawater magnesium oxide is expected to be about Rs 300 per tonne. Evidently the cost of production can be reduced by installing a larger capacity plant.

#### REFERENCES

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# Sorel Cement

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Magnesium oxychloride cement is chiefly favoured because it does not need long curing time, has high mechanical strength and can be laid on any sub-floor. The cement is light in weight, fire-resistant and is said to have germicidal properties. The method of manufacturing such cement in the country and its main uses are discussed.

Magnesium oxychloride also called 'Sorel Cement' after the name of the discoverer, is a self setting cement prepared from magnesium oxide, magnesium chloride and suitable fillers. Oxychloride cement is chiefly favoured because of its useful characteristics some of which are discussed below.

**Curing time.** The oxychloride cement does not require damp curing. The base floors made from this cement can be put into service 48 hr after laying.

**High strength.** The oxychloride cement concretes possess high early strength. The transverse, tensile and compressive strengths are 2300, 1000 and 7500 p.s.i. respectively for a correctly prepared mix.

**Sub-floor.** This cement can be laid on any kind of sub-floor, regardless of roughness and irregularities of the sub-floors.

**Miscellaneous.** The cement is light in weight, fire resistant, germicidal and has a low thermal conductivity and coefficient of thermal expansion.

## Uses

On account of these excellent properties oxychloride cements are used in factory sheds, hospitals, office rooms and railway compartments for jointless flooring. Tiles, glazed as well as mosaic, can be made from this cement. Other utility articles such as table tops, paperweights, wall-boards, etc. can also be made. On account of the unusually high bonding power, the oxychloride cement can be used in the preparation of artificial grinding stones, dental cement, and emery wheels etc.

## Raw materials

The raw material resources for the above industry are plentiful. India has large reserves of magnesite, some of which are of high quality suitable for refractory magnesia. Caustic, calcined magnesia obtained from magnesite is used as a source of magnesium oxide. The other raw material, viz. magnesium chloride is a by-product of salt



industry. With a production of 4.5 million tons of salt about one million tons of magnesium chloride are available, all of which is not recovered because of the limited market for this commodity. The popularization of the use of oxychloride cement in various industries mentioned above opens up the possibilities of the utilization of the by-product of salt industry. Again, large scale manufacture of the potassium fertilizers from bitterns will be producing a large quantity of magnesium chloride, which, if suitably utilized will contribute to the lowering of cost of these fertilizer materials.

### Scope

Due to various reasons, oxychloride cement has found only a limited use in India. In USA it is said that 100 million sq. ft of floors are laid every year. One of the largest consumers of this cement in India is the railways. There are some firms in India dealing in oxychloride cement. It is reported that annual turnover of one firm has increased from Rs 0.75 million in 1963-64 to Rs 0.995 million in 1964-65. There is thus a definite indication of the growth of magnesium oxychloride cement industry in the country.

There is a wide scope of expansion of sorel cement industry not only for domestic consumption but for export also. The statistics show that India is exporting millions of grinding stones and wheels to countries of South East Asia and Africa. These artificial stones can be made using oxychloride cement as a bonding material. The estimated cost of laying 100 sq. ft of jointless flooring 1 in. deep is Rs 125.

### Manufacture aspect

Although magnesium oxide obtained by light calcination of magnesite is at present used in oxychloride cement, alternate source such as seawater magnesium should be tried, so that the valuable magnesite is available either for refractories or for export. There are two methods for obtaining seawater magnesia. One is by the precipitation of magnesium hydroxide from magnesium salts present in bittern or directly from seawater using calcined limestone or dolomite; or by the calcination of magnesium chloride wherein, along with magnesium oxide, hydrochloric acid can also be recovered. The coast of Saurashtra and Kutch offers possibilities for the manufacture of magnesium oxide by precipitation. With a well developed salt industry plenty of soluble magnesium salts are available. There are some good deposits of high calcium limestone in this region. One of the abundant sources is at a place named Gorakhmudi where an estimated 3 lakh tons of limestone are available. The Porbandar limestone is widely used as a building material. The massive corallite available from the bed of the sea is white and porous and gives white lime on calcination. These limestones are quite pure ( $\text{SiO}_2$  0.22,  $\text{R}_2\text{O}_3$  0.17,  $\text{Fe}_2\text{O}_3$  0.05) and suitable for the manufacture of magnesium hydroxide. Although the processes are generally known the detailed techniques of manufacture will have to be worked out especially keeping in view the raw materials available in the region. Again the seawater magnesia will have to be suitably treated to bring it to satisfy the relevant specifications for oxychloride cement. There is still one more raw material which can possibly be used as a source of magnesia. This is dolomite; the magnesium oxide part of the dolomite can be used for oxychloride cement.









Price: Rs 1.50 Sh. 3/- \$ 0.50